

PATENT ABSTRACTS OF JAPAN

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(54) ACRYLIC EMULSION-TYPE TACKY AGENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an acrylic emulsion-type tacky agent having extremely excellent water resistance.

SOLUTION: This acrylic emulsion-type tacky agent is obtained by continuously dropping an emulsified monomer emulsified by adding 0.5-5 pts.wt. of a reactive nonionic emulsifier to 100 pts.wt. of a mixed monomer of 90-98wt.% at least one kind of (meth)acrylate expressed by the formula: $\text{CH}_2=\text{CR}_1\text{-COOR}_2$ (R1 is hydrogen or methyl group, R2 is a 4-14C alkyl group) with 2-10wt.% at least one kind of monomer selected from among a carboxylic group-containing monomer, an amide group-containing monomer and a hydroxyl group-containing monomer and subjecting to an emulsion polymerization at a polymerization temperature of $\leq 75^\circ\text{C}$.

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CLAIMS

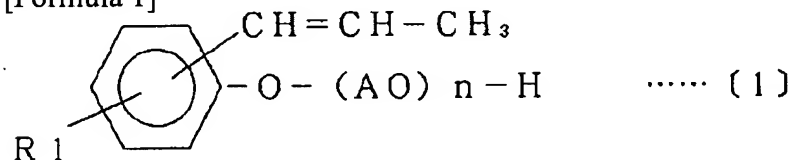
[Claim(s)]

[Claim 1] 90 - 98 % of the weight (meta) of acrylic ester more than a kind expressed with general formula $\text{CH}_2 = \text{CR}_1 - \text{COOR}_2$ (hydrogen or a methyl group, and R_2 show the alkyl group of carbon numbers 4-14 among a formula, as for R_1), In the 2 - 10 % of the weight [of monomers more than a kind chosen from a carboxyl group content monomer, an amide group content monomer, and a hydroxyl-group content monomer] mixed monomer 100 weight section The acrylic emulsion mold binder characterized by the emulsified emulsification monomer which carried out reactant Nonion emulsifier 0.5-5 weight section addition being dropped continuously, and coming to carry out an emulsion polymerization at the polymerization temperature of 75 degrees C or less.

[Claim 2] The acrylic emulsion mold binder according to claim 1 with which the reactant Nonion emulsifier is characterized by being [of the following general formula [1] and [2]] a kind at least.

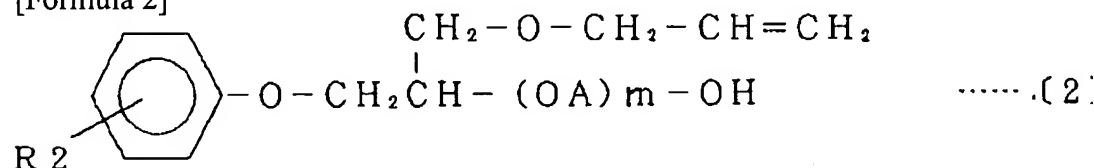
[0001]

[Formula 1]



[0001]

[Formula 2]



[0001] However, R_1 and R_2 are the alkyl group of carbon numbers 6-18, an alkenyl radical, or a permutation aralkyl radical.

The integer A of 20-100 is m, and n is the alkylene group or permutation alkylene group of carbon numbers 2-4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the acrylic emulsion mold binder excellent in the water resisting property.

[0002]

[Description of the Prior Art] The acrylic binder excellent in the balance and endurance of physical properties has spread widely instead of natural rubber or a synthetic-rubber system binder in recent years. An acrylic emulsion mold binder has come to be widely used in that the problem especially in a public nuisance and an environmental side is avoidable. However, since the acrylic emulsion mold binder is using the emulsifier, it has the problem that a water resisting property is bad and produces a fall or nebula of adhesion or cohesive force at the time of water immersion, or the time of highly humid.

[0003] As what improves the above-mentioned water resisting property, although it is an anticorrosion paint, the water-dispersion resin constituent of the copolymer obtained by carrying out the emulsion polymerization of the acrylic-acid (meta) alkyl ester system monomer under existence of a reactant emulsifier is indicated by JP,7-13207,B. Since it excels in gloss, a water resisting property, spraying nature, etc., this thing is used as a vehicle for anticorrosion paints.

[0004]

[Problem(s) to be Solved by the Invention] According to the water-dispersion resin constituent given in the above-mentioned official report, since the reactant emulsifier is used, a water resisting property improves considerably, but also after carrying out spreading desiccation of this at an object, the functional group of ionicity remains in a binder. Therefore, as a water resisting property which can be equal to water immersion etc., it is inadequate.

[0005] It aims at offering the acrylic emulsion mold binder with which this invention cancels the above-mentioned conventional trouble, and it excels in a water resisting property and stability, and milkiness cannot take place easily.

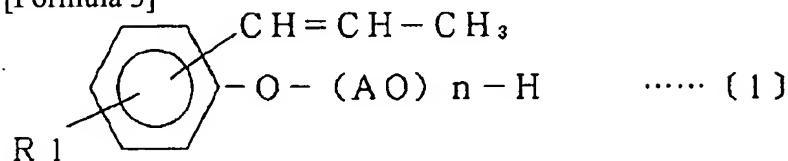
[0006]

[Means for Solving the Problem] this invention acrylic emulsion mold binder according to claim 1 90 - 98 % of the weight (meta) of acrylic ester more than a kind expressed with general formula $\text{CH}_2=\text{CR}_1-\text{COOR}_2$ (hydrogen or a methyl group, and R_2 show the alkyl group of carbon numbers 4-14 among a formula, as for R_1), In the 2 - 10 % of the weight [of monomers more than a kind chosen from a carboxyl group content monomer, an amide group content monomer, and a hydroxyl-group content monomer] mixed monomer 100 weight section The emulsified emulsification monomer which carried out reactant Nonion emulsifier 0.5-5 weight section addition is dropped continuously, and it is characterized by coming to carry out an emulsion polymerization at the polymerization temperature of 75 degrees C or less.

[0007] Moreover, this invention acrylic emulsion mold binder according to claim 2 is characterized by the reactant Nonion emulsifier according to claim 1 being [of the following general formula [1] and [2]] a kind at least.

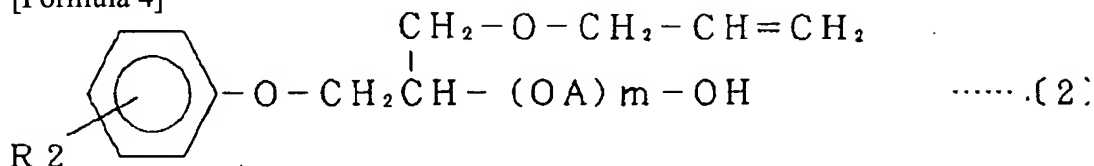
[0008]

[Formula 3]



[0009]

[Formula 4]



[0010] However, R1 and R2 are the alkyl group of carbon numbers 6-18, an alkenyl radical, or a permutation aralkyl radical.

The integer A of 20-100 is m, and n is the alkylene group or permutation alkylene group [0011] of carbon numbers 2-4. Although n-butyl acrylate, 2-ethylhexyl acrylate, iso octyl acrylate, iso nonyl acrylate, laurylacrylate, etc. are mentioned in this invention as alkyl acrylate whose carbon numbers of an alkyl group are 4-14, these (meta) acrylic ester is used in 90 - 98% of the weight of the range in the monomer whole quantity. (Meta) If the amount of acrylic ester becomes less than 90 % of the weight, the adhesion of a binder will decline, and if it exceeds 98 % of the weight, the cohesive force of a binder will decline.

[0012] As a carboxyl group content monomer, an acrylic acid (meta), a maleic acid, an itaconic acid, etc. are mentioned. As an amide group content monomer, acrylamide (meta), N-isopropyl acrylamide, N-vinyl pyrrolidone, N-vinyl caprolactam, etc. are mentioned. As a hydroxyl-group content monomer, 2-hydroxyethyl (meta) acrylate, 4-hydroxy butyl acrylate, etc. are mentioned. One or more sorts of monomers chosen from these are used as 2 - 10 % of the weight in [all] a monomer. If these polar monomers become less than 2 % of the weight, cohesive force will become low, if it exceeds 10 % of the weight, cohesive force will become high too much and adhesion will decline.

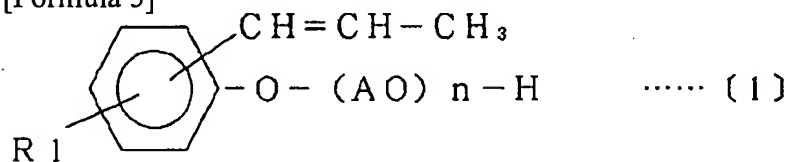
[0013] Even if it copolymerizes the monomer of styrene, vinyl acetate, methyl (meta) acrylate, ethyl (meta) acrylate, etc. which can be copolymerized if needed, it does not interfere with the above-mentioned monomer. Moreover, even if it copolymerizes a macro monomer, it does not interfere.

However, the macro monomer should consider as 25 or less % of the weight in [all] the monomer.

[0014] Although it can be used as a reactant Nonion emulsifier if it has a copolymeric partial saturation radical, it is required to use at least one sort expressed with the following general formula [1] and [2].

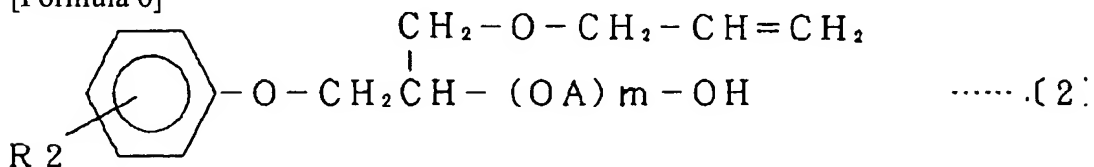
[0015]

[Formula 5]



[0016]

[Formula 6]



[0017] m in a formula and n are the integers of 20-100 here. The cloudy point of an emulsifier becomes it low that the value of m and n is less than 20, surface activity capacity declines with heating at the time of a polymerization, and polymerization stability gets worse remarkably. The addition of a reactant emulsifier is 0.5 - 5 weight section to all the monomer 100 weight sections, and is 0.5 - 3 weight section preferably. If fewer than the 0.5 weight section, polymerization stability will fall, and if 5 weight sections are exceeded, a water resisting property will fall.

[0018] Temperature at the time of carrying out an emulsion polymerization is performed below 75 degrees C. If it exceeds 75 degrees C, the surface activity capacity of the Nonion nature emulsifier will decline, and polymerization stability will get worse remarkably.

[0019] The redox system polymerization initiator which used together water-soluble azo compounds, such as persulfate, such as ammonium persulfate, and azobis cyano valerianic acid, or the hydrogen peroxide, and the reducing agent as a polymerization initiator can use it suitably. The amount of the polymerization initiator used has desirable 0.01 - 1 weight section to all the monomer 100 weight sections, and is the 0.03 - 0.5 weight section more preferably. Since a cyano group may remain if a water-soluble azo compound is used, cautions are required.

[0020] The acrylic emulsion mold binder of this invention may adjust molecular weight using chain transfer agents, such as dodecyl mercaptan, and may copolymerize polyfunctional (meta) acrylate etc. Moreover, viscosity controlling agents, such as polyacrylic acid and water-soluble urethane resin, antiseptics, etc. may be added. Furthermore, according to the application of a binder, tackifiers, such as a rosin system, a rosin ester system, a terpene system, and a petroleum resin system, may be added.

[0021] Since the acrylic emulsion mold binder of this invention is a water dispersion, it needs to raise physical stability, to use PH regulator, in order not to start poor coating, such as **** by an aggregate generating in coating, and unevenness, and to adjust to PHs 6-9.

[0022] A bridge may be constructed by adding a cross linking agent to the binder of this invention. As a cross linking agent, things, such as an aziridine system, an isocyanate system of a block or self-emulsifiability, a carbodiimide system, and a metal system, are used.

[0023] Although especially the application of the acrylic emulsion mold binder of this invention is not limited, there are adhesive tape, a pressure sensitive adhesive sheet, a pressure sensitive adhesive label, a pressure sensitive adhesive double coated tape, etc., for example. Although especially limitation does not have these base materials, either, foam, such as films, such as polyethylene terephthalate and extension polypropylene, polyurethane, polyethylene, and rubber, paper, cloth, a nonwoven fabric, etc. are mentioned, for example.

[0024] (Operation) Since only the Nonion nature emulsifier is being used for the acrylic emulsion mold binder of this invention as an emulsifier, the functional group of the ionicity by the emulsifier does not exist in the paint film formed after coating desiccation in this. Moreover, since the Nonion nature emulsifier is reactivity, the emulsifier which separated in the formed paint film does not exist. The binder layer formed by carrying out coating desiccation by these things becomes that whose water resisting property improved remarkably. Furthermore, since there is no functional group of ionicity in an emulsifier, the aggregate by the ion shock does not generate. Thereby, a good paint film is formed.

[0025]

[Embodiment of the Invention] The example of the acrylic emulsion mold binder of this invention is explained below.

(Example 1) The ion-exchange-water 60 weight section which dissolved the ammonium persulfate 0.1 weight section was supplied in the 1l. reaction container equipped with a thermometer, an agitator, a reflux cooling pipe, and nitrogen gas installation tubing, and it warmed at 70 degrees C under nitrogen-gas-atmosphere mind. The following were prepared as monomer mixture.

n-butyl acrylate 76 weight sections 2-ethylhexyl acrylate 20 weight sections acrylic acid Two weight sections methacrylic acid Two weight sections n-dodecyl mercaptan The 0.05 weight sections [0026] The emulsification monomer which added the propenyl radical addition polyoxyethylene nonylphenyl ether (30 Dai-Ichi Kogyo Seiyaku Co., Ltd. make and trade name "Aqualon RN-30" EO addition mols) 1 weight section and the ion-exchange-water 40 weight section as a reactant Nonion emulsifier, and

carried out mixed stirring and which was emulsified to the above-mentioned mixed monomer was taught to the tap funnel. Keeping said reaction container at 70 degrees C, the above-mentioned emulsification monomer was dropped over 3 hours, and the polymerization was performed. It maintained at 70 degrees C after dropping termination of an emulsification monomer for 1 hour, and was made to react at 75 more degrees C for 3 hours. After cooling the above-mentioned polymerization liquid at 30 degrees C or less, it neutralized by aqueous ammonia solubility 25%, and the acrylic emulsion mold binder of this invention was obtained. Solid content was 50%.

[0027] (Example 2) The acrylic emulsion mold binder was obtained like the example 1 except having made the propenyl radical addition polyoxyethylene nonylphenyl ether into 2 weight sections.

[0028] (Example 3) The acrylic emulsion mold binder was obtained like the example 1 except having used it, having changed the reactant Nonion emulsifier to the allyl group addition polyoxyethylene nonylphenyl ether (20 Asahi electrification company make and trade name "ADEKA rear soap NE-20" EO addition mols) 1 weight section.

[0029] (Example 1 of a comparison) The acrylic emulsion mold binder was obtained like the example 1 except having made the emulsifier into the propenyl radical addition polyoxyethylene nonylphenyl ethereal sulfate ammonium salt (ten Dai-Ichi Kogyo Seiyaku Co., Ltd. make and trade name "Aqualon HS-10" EO addition mols) 1 weight section which is a reactant anion emulsifier.

[0030] (Example 2 of a comparison) It was made to react for 3 hours at the time of emulsification monomer dropping, keeping reaction temperature at 70 degrees C, and it obtained the acrylic emulsion mold binder like the example 1 except having considered as 2 hours at 80 degrees C after that by 70 degrees C for 1 hour.

[0031] The emulsion property of the binder obtained in the above-mentioned examples 1-3 and the examples 1-2 of a comparison was measured according to the approach shown below.

(1) 1.5g of emulsions was taken in the measurement aluminum cup of emulsion property ** solid content, it dried at 110 degrees C for 3 hours, and solid content was computed by the degree type. The solid content (%) = (dry weight (g)/1.5 (g)) x 100 ** polymerization stability emulsion was filtered at the wire gauze made from stainless steel of 100 meshes, and after drying at 110 degrees C for 3 hours, the rate to the total-solids weight of the residue on a wire gauze was computed by the degree type.

残渣の乾燥重量 (g)

$$\text{重合安定性 (\%)} = \frac{\text{残渣の乾燥重量 (g)}}{\text{エマルジョン総重量 (g)} \times \text{固形分 (\%)}} \times 100$$

** Add 25g of ion exchange water to physical stability emulsion 25g, and it is referred to as 50g. The Merlon mold mechanical stability testing machine (consonance surface chemistry company make, trade name "an emulsion latex mechanical stability-characteristics observation-recorder CMS-A mold") is used, and it is 10kg/cm². After rotating for 5 minutes by rotational frequency 1000rpm under a pressure, The rate to the total solids of the dry weight after filtering the aggregate in a container at the wire gauze of 100 meshes and drying at 110 degrees C for 3 hours was computed by the degree type.

残渣の乾燥重量 (g)

$$\text{機械安定性 (\%)} = \frac{\text{残渣の乾燥重量 (g)}}{25 \text{ (g)} \times \text{固形分 (\%)}} \times 100$$

[0032] ** The adhesive tape which carries out spreading desiccation of the milkiness-proof sex-test examples 1-3 and example 1 of comparison - 2 ***** acrylic emulsion mold binder at a polyethylene terephthalate film (thickness of 38 micrometers), and has the binder layer whose thickness is 25 micrometers was produced, the same polyethylene terephthalate film as a binder stratification plane was stuck, and the milkiness-proof sex test was performed using this sample.

[0033] The sample was cut off in 100mmx25mm magnitude, and the Hayes value was measured using the hazemeter (the Tokyo Denshoku Co., Ltd. make, trade name "MODEL TC-H111DP").

Subsequently, the Hayes value immediately after being immersed in underwater [23-degree C] for 48

hours, and taking out the above-mentioned sample was measured. The above result is shown in Table 1.

[0034]

[Table 1]

		実施例			比較例	
		1	2	3	1	2
エ マ ン ル 特 性	固形分 (%)	50	51	50	50	48
	重合安定性 (%)	0.01	0.01	0.02	0.01	1.52
	物理的安定性 (%)	0.01	0.01	0.01	0.01	0.01
耐 白 化 性	ヘイズ値					
	ブランク (%)	8.5	8.4	8.5	8.6	8.4
	水浸漬後 (%)	10.1	10.6	10.0	15.0	10.0
	差 (%)	1.6	2.2	1.5	6.4	1.6

[0035] By Table 1, the thing of examples 1-3 is equal also about which evaluation criteria. However, since the thing of the example 1 of a comparison used the reactant anion emulsifier, its milkiness-proof nature is large, and since the thing of the example 2 of a comparison makes polymerization temperature high and carries out a polymerization, it is understood that polymerization stability is bad.

[0036]

[Effect of the Invention] this invention acrylic emulsion mold binder is the above configuration, since only the reactant Nonion emulsifier is used as an emulsifier, the functional group of ionicity does not exist in the binder layer using this, and the emulsifier which separated does not exist. Therefore, a binder layer becomes that whose water resisting property improved remarkably. Furthermore, since there is no functional group of ionicity in an emulsifier and the aggregate by the ion shock does not generate, a good paint film is formed. Therefore, since the adhesive tape using this binder etc. has a high water resisting property, it can be used also for the field which was not able to be applied by the thing using the conventional acrylic binder.

[Translation done.]